



Acrylamide formation and aroma evaluation of fried pepper sauce under different exogenous Maillard reaction conditions

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ABSTRACT

To explore the impact of the Maillard reaction on fried pepper sauce (FPS) flavor and safety quality, acrylamide and volatile organic compounds (VOCs) were measured in FPS. Acrylamide was detected in 10 Maillard treated groups and a total of 110 VOCs were identified, mainly aldehydes, ketones, alcohols, acids, etc., but the content of each group differed. Partial least squares discriminant analysis showed that acrylamide in white sugar-sodium glutamate group and xylose-soy peptide group processing accumulated most acrylamide and least VOCs; Lactose-glycine, lactose-cysteine, lactose-soy peptide, and white sugar-glycine groups were positively correlated with typical Maillard reaction product (2,3-Dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-One); Xylose-glycine, xylose-cysteine, and white sugar-cysteine groups were weakly correlated with typical products, but positively correlated with most VOCs, whereas white sugar-cysteine group lipids showed high oxidation levels. Although white sugar-soy peptide group is not harmful on acrylamide, it has little correlation with VOCs with large responses. Conventional excipient group aroma is relatively simple with a fresh fatty taste, whereas xylose-glycine, xylose-cysteine, xylose-soy peptide, lactose-glycine, and white sugar-cysteine groups all present basic fresh and fatty tastes; lactose-cysteine group has a fruity base note; and lactose-soybean peptide, white sugar-glycine, and white sugar-soybean peptide groups have a fruity base note on an unpleasant fatty aroma. Therefore, processing different exogenous Maillard reaction substrates can achieve FPS aroma regulation and reduce acrylamide harm.

Introduction

Fried pepper sauce (FPS, *Capsicum annum* L.) is a common local condiment in China for serving and seasoning, comprising dried pepper powder, peanuts, sesame, soybeans, salt, sugar, and monosodium glutamate with other auxiliary materials from deep frying. Deep frying is the key technology for FPS. Fat and food components undergo physical and chemical changes due to heat transfer in frying (Dobarganes, Márquez-Ruiz, & Velasco, 2015), which imparts color and aroma to the fried foods. Food components such as protein, polysaccharides, lipids, etc., decompose or react with each other during frying to form aromatic substances, etc. Food and frying oil components (including decomposition products from frying oil components) react together to generate

aromatic substances, etc. The pepper acquires a unique spicy taste after being fried and is rich in volatile aroma components (VOCs), such as enterpenoids and esters (Liu, Wu, Wang, & Tang, 2013). However, Deep frying can cause lipid oxidation and degradation and Maillard reaction (MR) of food components at high temperatures.

Acrylamide can be formed by acrolein or acrylic acid in a fried system with less sugar (Yasuhara, Tanaka, Hengel, & Shibamoto, 2003). The acrolein or acrylate formed by lipid oxidation can form acrylamide by amino dehydroxyl reaction in the presence of ammonia (Daniali, Jinap, Hajeb, Sanny, & Tan, 2016; Smith & March, 2001). Simultaneously, acrylamide production in hot-processed food comes from the Maillard reaction, and asparagine-based amine (Asn) is the main precursor of acrylamide (Mottram, Wedzicha, & Dodson, 2002; Stadler,

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Blank, Varga, et al., 2002). Reduced sugars and asparagine provide the molecular skeleton for the final formation of acrylamide (Adam, Benjamin, David, & Stephen, 2003; Zyzak, Sanders, Stojanovic, et al., 2003). Preliminary research into potential FPS hazards at high temperature found that FPS undergoes lipid oxidation and Maillard reaction to form acrylamide in high-temperature frying (Song, Ding, Wu, et al., 2021). Acrylamide has adverse effects on the human body and is classified as Group 2A by the International Agency for Research on Cancer (IARC, 1994). Therefore, it is essential to regulate FPS acrylamide formation during high temperature processing.

The MR is a series of non-enzymatic chemical reactions between carbonyl groups (mainly carbohydrates) and amino compounds of biological origin (Mossine & Mawhinney, 2010). It imparts unique flavor and color to food, is one of the most common reactions in thermal processing (Liu, Liu, He, Song, & Chen, 2015; Noda, Yamada, & Murata, 2015), and is widely used in food baking, coffee processing, flavor production, etc. (Ogasawara, Katsumata, & Egi, 2006). However, MR can also lead to fat deterioration and the acrylamide formation (Tamanna & Mahmood, 2015). FPS ingredients (dried pepper powder, white sugar, sodium glutamate, etc.) are important factors for MR occurrence during high-temperature frying. Conventional excipients (white sugar and sodium glutamate) have important impacts on pepper color and aroma and acrylamide formation.

Different sugar types participate in MR at different rates. Hamdi, Nasri, Azaza, Li, and Nasri (2020) found the reaction rate was aldose > ketohexose > aldose, because different amino acids and sugars reacted to produce different flavor compound amounts and types. The different amino acids and sugars can be selected to provide specific flavors and flavor substances (Yu, Zhang, & Zhang, 2018). Thus, different amino acids and sugars participate in MR with different efficiencies, and acrylamide and VOC formations also differ. Therefore, processing foods with different exogenous MR substrates influences flavor quality and acrylamide formation.

Although MR aromatization has been widely used in food processing, studies on MR application for fried pepper sauce is rare. The pepper itself may contain potential MR substrates (Yu, Zhang, & Zhang, 2018). Combining MR with frying has practical significance to explore powerful measures to simultaneously enhance FPS aroma and reduce acrylamide. Few studies have compared acrylamide and aroma enhancement effects for different MR substrates. Therefore, this article uses the conventional excipient FPS formula as a control to investigate effects from addition external Maillard substrates on acrylamide formation and VOC formation in MR treated samples. Different MR substrate effects on aroma production, acrylamide prevention, and FPS control were evaluated. We explored effective ways to improve product safety and quality by reducing FPS acrylamide content while ensuring characteristic flavor, and provide reference guidance for FPS product quality improvements for enterprises.

Materials and methods

Materials

Dried red peppers (*C. annuum* L. var. India 2), rapeseed oil, salt, sodium glutamate (food grade), and sugar were purchased from a local supermarket in Guiyang, China. All peppers were at commercial maturity and were washed, and drained. We selected relatively uniform size, color, and weight, peppers; free from visible blemishes, disease and physical damage. The dried red peppers were ground using a high-speed multifunction pulverizer (RRH-250, Shanghai Yuanwo Trading Co., Ltd., Shanghai, China) as to obtain red pepper powder.

Maillard-treated fried pepper sauce production

We placed a wok, a bowl-shaped frying pan used typically in Chinese cooking, on a heated plate (JOANLAB HP-1000 W, Joan Lab Equipment

Co., Ltd., Zhejiang, China), added rapeseed oil, raised the oil temperature to 270 °C, and then reduced it to the required stir-fry temperature (170 °C). Temperature was controlled to within ±5 °C, and we added dried pepper powder (rapeseed oil:dried pepper powder = 3:1 (w/w), for 100% rapeseed oil content), 5.0% salt, and different Maillard fragrance substrates (different sugars and amino acids at 1:1 ratio); and the mixture was stir-fried for 5 min. After cooling to room temperature, the FPS was bottled and then stored at 4 °C in 250 mL bottles. All experiments were performed in triplicate. Samples formed ten groups depending on the Maillard additives as shown in Table 1.

HS-GC-TOF-MS analysis

We added 2 mL oil sample to 20 mL headspace vial, and insert an extraction head into the headspace. SPME (50/30umCAR/PDMS/DVB, Supelco-57329U) fiber was exposed to the headspace of at 60 °C for 30 min, then inserted to the GC injector for desorption at 250 °C for 3 min while operating the instrument to collect data. Upper gas was injected into the GC-TOF-MS (Pegasus HRT 4D Plus (LECO, Michigan, USA) equipped with a DB-Wax column (30 m × 0.25 mm × 0.25 μm, Agilent) maintained at 40 °C for 3 min, and then warmed to 230 °C at 10 °C/min and maintained for 6 min. Injector temperatures were set at 250 °C. Helium (purity > 99.999%) was used as carrier gas at 1 mL/min and ionization was performed under electronic impact (EI) with 70 eV electron ionization source and 200 °C ion source temperature. Emission current = 1 mA, multiplier voltage = 2000 V, and interface temperature = 250 °C. One-dimensional full scan mode with a scan range 33–450 *m/z* was adopted with 200 spec/s acquisition rate.

We calculated VOC retention index RI using *n*-ketones C4–C9. VOC peaks in the total ion chromatogram were retrieved by mass spectrometry and checked against NIST 2005 and Wiley 275 standard mass spectra to identify specific fried pepper sauce VOCs. Peak area normalization was used for quantitative analysis using spectral library workstation data to obtain relative content for each chemical component in the volatile flavor substances.

Relative odor-activity

To evaluate aromatic compound contributions to fried pepper sauce, relative odor activity (ROAV) was calculated following Liu, Zhou, & Xu (2008), using the ROAV_{stan} that contributes the most to overall sample flavor as comparator for other components, A,

$$ROAV_A \approx 100 \times \frac{C\%_A}{C\%_{stan}} \times \frac{T_{stan}}{T_A} \quad (1)$$

where C% is relative content (%), and T is detection threshold from published odor threshold in oil (van Gemert, 2011). All components have ROAV ≤ 100, and greater ROAV implies greater contribution to overall sample flavor. Generally, aromatic compounds with ROAV > 1 may have a significant contribution to fried pepper sauce, whereas compounds with OAV < 1 contribute less.

Table 1
Fried pepper sauce with different Maillard reaction substrates.

Count	Compound
A	white sugar and sodium glutamate (control)
B	xylose and glycine
C	xylose and cysteine
D	xylose and soy peptides
E	lactose and glycine
F	lactose and cysteine
G	lactose and soybean peptide
H	white sugar and glycine
I	white sugar and cysteine
J	white sugar and soybean peptide

Acrylamide determination

Acrylamide was determined by standard liquid chromatography-tandem mass spectrometry (LC-MS/MS) (GB 5009.204-Chinese National Standards 2014, 2014). Briefly, 12 g pepper solids was added to 10 μ L 13C3-acrylamide solution (10 mg/L) as internal standard, and 10 mL ultrapure water, then vortexed for 30 min, and centrifuged at 4000g for 10 min. Supernatant was collected for analysis by LC-MS/MS. The equipment comprised an Agilent SB14037 LC-MS/MS (Agilent Technologies Co., Ltd., Palo Alto, CA, USA) with Hypersil GOLD C18 column (2.1 \times 100 mm, 1.9 μ m; Thermo Fisher Scientific Co., Ltd., Waltham, MA, USA). A standard curve was constructed for acrylamide quantification,

$$y = 0.00525 \times -0.000764; R^2 = 0.9999.$$

The mass spectrometer was operated using electrospray ionization in positive ion mode (ESI+) with capillary voltage = 3.5 kV, ion source temperature = 80 $^{\circ}$ C, desolvent gas temperature = 300 $^{\circ}$ C, and hence ion collision energy = 6 eV. Detection was performed in the multiple reaction monitoring mode. Mass transitions monitored were acrylamide (72 m/z), parent ion (55 m/z), and quantitative ion (7244 m/z); and 13C3-acrylamide (75 m/z), parent ion (58 m/z), and quantitative ion (7545 m/z).

Data analysis

All experiment were performed in triplicate. Diagrams were drawn using Origin 2019 (OriginLab, Northampton, MA), and partial least squares discriminant analysis (PLS-DA) was employed to visualize differences between samples using SIMCA (V14.1, Umetrics AB, Umeå, Sweden).

Results and discussion

Acrylamide content in Maillard treated fried pepper sauce

Fig. 1 compares acrylamide content for the different Maillard substrate combinations detailed in Section “Maillard-treated fried pepper sauce production”, with conventional excipient (white sugar-sodium glutamate) as control.

Detected acrylamide level for each treatment group = 9.5–14.0 mg/kg,

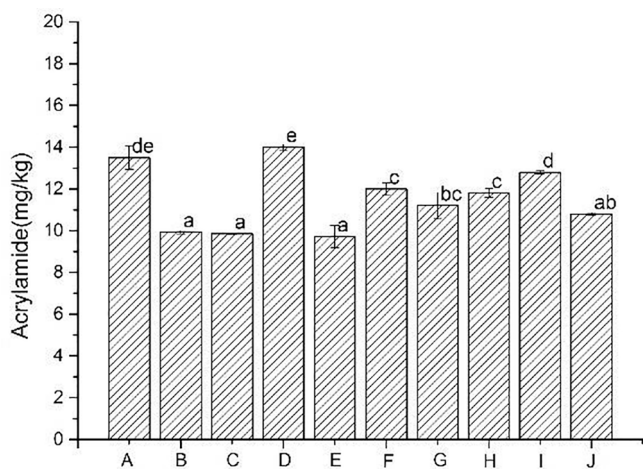


Fig. 1. Acrylamide content in fried pepper sauce for different carbonyl ammonium substrates: (A) sugar and sodium glutamate, (B) xylose and glycine, (C) xylose and cysteine, (D) xylose and soy peptides, (E) lactose and glycine, (F) lactose and cysteine, (G) lactose and soybean peptide, (H) sugar and glycine, (I) sugar and cysteine, and (J) sugar and soybean Peptide. Lowercase letters indicate significant differences between treatments ($P < 0.05$).

kg, with group D higher than the control group. There is no significant difference between groups D, I, and A ($P > 0.05$), and detected acrylamide levels for all other groups are significantly lower than for conventional excipients ($P < 0.05$). Acrylamide content differences among the treatment groups indicates that different Maillard reaction substrates participate in the acrylamide production pathway. Asparagine produces extremely small amounts of acrylamide when present in the fried system and heated alone (Granvogl, Jezussek, Koehler, & Schieberle, 2004). The carbonyl compounds can be degraded by Strecker, or participate in the MR to promote acrylamide production (Zamora, Delgado, & Hidalgo, 2009). Further, asparagine can react with the active carbonyl compounds to form the corresponding Schiff base, which then decarboxylated and eliminated to form acrylamide (Hidalgo, & Zamora, 2004). In addition, carbonyl compounds formed by the oil oxidation in frying systems can also promote acrylamide formation (Yasuhara, Tanaka, Hengel, & Shibamoto, 2003). Meanwhile, asparagine can react with the reducing sugar of food composition to form acrylamide (Ledl, & Schleicher, 2010). Therefore, acrylamide was highly detected in each treatment group.

A Maillard reaction substrate with smaller production could be an alternative to conventional white sugar and sodium glutamate adjuvant aroma substrate, including xylose and glycine, xylose and cysteine, lactose and glycine, lactose and cysteine, lactose and soy peptide, white sugar and glycine, and white sugar and soy peptide, where lactose and glycine acrylamide exhibited lowest detected level. The reason for this difference is the different sugar substrates involved in the MR have different reactivities (Dufosse, Laroque, Guerard, Inisan, Berger, & Vouland, 2008; Meinert, Schaefer, Bjerregaard, Aaslyng, & Bredie, 2009), and the acrylamide content can be significantly reduced by adding some amino acids such as cysteine and glycine (Liu, Chen, Man, Dong, & Hu, 2011; Sadd, Hamlet, & Liang, 2008). Since exogenous MR is widely used in various food flavoring technologies, further analyze the aroma effect of different reaction substrates has great significance for food processing.

HS-GC-TOF-MS analysis for volatile flavor substances in Maillard treated fried pepper sauce

Fig. 2 shows GC-TOF-MS results for the 10 treatment groups. There were 10 main types of 110 volatile compounds in Maillard treated fried pepper sauce (MTFPS) samples, including aldehydes (36), ketones (16), alcohols (7), furans and pyrans (4), acids (5), alkenes (6), hydrocarbons (4), pyrazines and pyrosirels (4), esters (6), and the others (6).

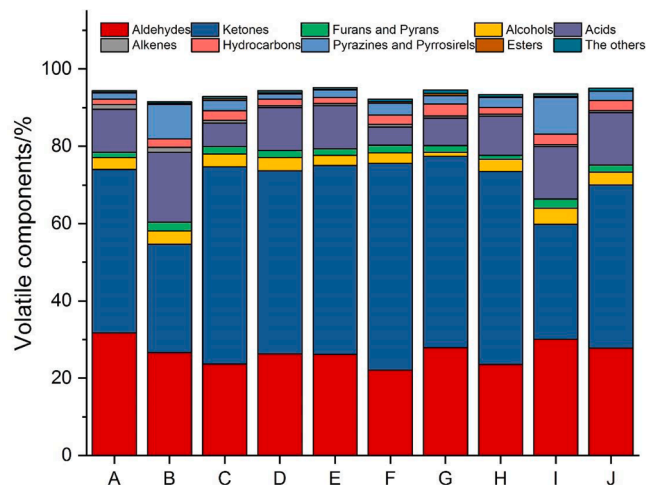


Fig. 2. Fried pepper sauce Volatile component type for different carbonyl ammonium substrates: (A) sugar and sodium glutamate, (B) xylose and glycine, (C) xylose and cysteine, (D) xylose and soy peptides, (E) lactose and glycine, (F) lactose and cysteine, (G) lactose and soybean Peptide, (H) sugar and glycine, (I) sugar and cysteine, and (J) sugar and soybean peptide.

(13), pyrazines and pyrroles (12), esters (5), and others (6), where (n) represents the number of distinct VOCs identified, confirming that MTFPSs are rich in flavor compounds. The more VOCs in each group are Groups E, G and J, with other groups having \leq group A, indicating that FPS volatility for lactose and glycine, lactose and soy peptide, and white sugar and soy peptide groups is richer than the conventional excipient. Because food lipid acyl group degradation under thermal oxidation conditions first forms primary oxidation compounds, including some acyl chains that support hydroperoxy or hydroxyl groups, and

conjugated dieny systems.

At higher temperatures, increased hydroperoxide concentration increases oxygen availability, and Maillard reactions reduce hydroperoxides and aldehyde, epoxide, and alcohol formation. However, the content of highly reactive aldehydes content decreases under deep frying conditions, e.g. (E, E)-2,4-alkyl (Mancebo-Campos, Fregapane, & Salvador, 2010). Lipid oxidation under high temperature conditions also produces short-chain fatty acids (Niu, Liang, Zhang, Jiang, Wang, & Shang, 2014). Therefore, the relative content of various substances is

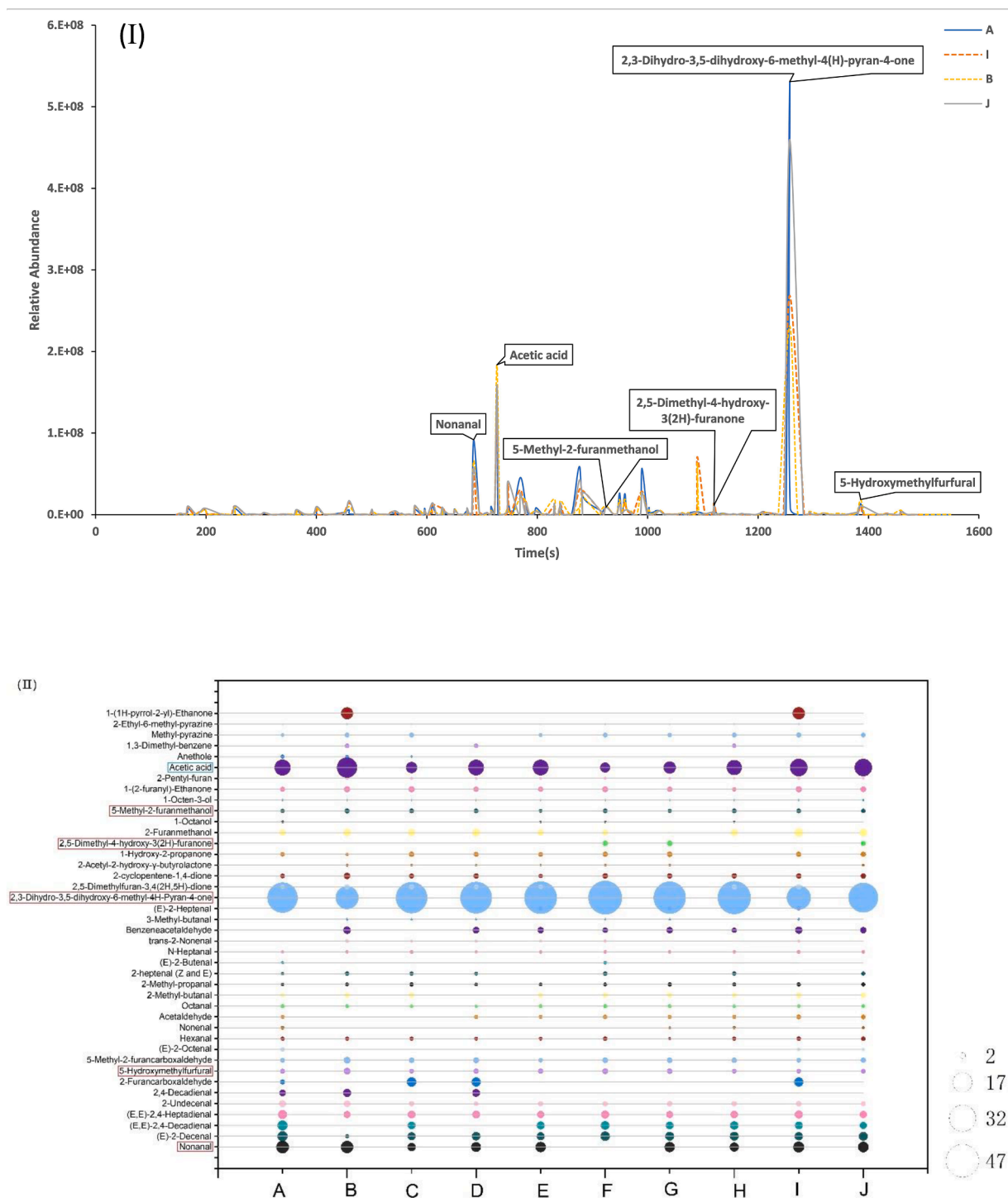


Fig. 3. Total ions chromatograph(I) and volatile components(II) in fried pepper sauce with different carbonyl ammonium substrates: (A) sugar and sodium glutamate, (B) xylose and glycine, (C) xylose and cysteine, (D) xylose and soy peptides, (E) lactose and glycine, (F) lactose and cysteine, (G) lactose and soybean Peptide, (H) Sugar and glycine, (I) sugar and cysteine, and (J) sugar and soybean peptide.

dominated by ketones (28–53%), aldehydes (22–31%), and acids (4–18%). Groups C, E, F, and G have more aldehydes, ketones, and lower acid content compared with group A, whereas groups B, I, and J have less aldehydes and ketones and higher acid content. Thus, MR occurrence and lipid oxidation degree differ for the 10 treatment groups: Xylose and cysteine, lactose and glycine, lactose and cysteine, and lactose and soybean peptide groups are more conducive to MR, compared with conventional adjuvant, and xylose and glycine, white sugar and cysteine, white sugar-soy peptide lipid oxidation level is higher. This difference is due to antioxidant properties for some MR products (Franciso & Morales, 2001; Korkmaz, Atasoy, & Hayaloglu, 2021).

Fig. 3 shows detailed VOC detection, separation, and identification results for the MTFPS samples included 66, 65, 71, 67, 73, 70, 72, 65, 71, and 67 VOC types in each group. The most common VOCs = lactose and glycine, lactose and soy peptide, xylose and cysteine, and white sugar and cysteine, whereas xylose and glycine and white sugar and glycine are less common than conventional excipient. Similarly, aldehydes, ketones, and acids are the main substances detected in each group. Nonanal (3–6%) and acetic acid (4–18%) have relatively high relative content in MTFPSs, and are important VOCs in oil oxidation. These two compounds may be produced by both carbohydrate metabolism and thermal processes (Korkmaz, Hayaloglu, & Atasoy, 2017). Nonanal has the fat aroma of beef tallow, orange and rose aroma when diluted, its threshold is low (1 µg/kg), and it may have a greater contribution to FPS flavor. Although acetic acid has a rancid taste, its threshold is relatively high (22,000 µg/kg), and it may not manifest an odor (Liu, Zhou, and Xu, 2008; Zhao, Ding, Xu, Gu & Ding, 2018). Aldehydes are important for volatile aroma formation due to their low perception threshold, the remaining aldehydes will be analyzed by ROAV.

MR products were detected in each treatment group. Ketones have significant contribution to VOCs, and relative content for 2,3-Dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one, a typical product from all Maillard reaction systems containing hexoses, is very high for all treatment groups (22–48%). Different hexoses and Amadori products first form sugar degradation products and the important Maillard precursor 1-deoxyosone as cyclic hydroxyfuranones and hydroxy pyranone forms in solution.

Intermediate hydroxy pyranone formed from monosaccharides can further produce 2,3-Dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one. It has a hay aroma, and although the aroma is weak, it can have important effects on FPS flavor due to its high relative content. 5-Hydroxymethylfurfural (HMF) and 3-hydroxy-2-methyl-4H-Pyran-4-one (maltol) are also Maillard reaction products, and relative HMF content is higher than maltol for each treatment group. This is probably due to different reducing sugar types in MR: HMF is formed first and maltol can be directly formed from disaccharides and Amadori compounds. However, maltol is only formed under basic and neutral conditions from disaccharides with free C-6 hydroxyl groups on the reducing sugar (Yaylayan & Mandeville, 1994). After dehydration promoted by the acidic environment in the presence of oxygen, HMF produces 5-methyl-2-Furancarboxaldehyde and 2,5-Diformyl furan (content for each group is very low and was not explicitly measured) (Cutzach, Chatonnet, & Dubourdieu, 1999). 5-methyl-2-Furancarboxaldehyde was detected in each treatment group, therefore, HMF may undergo dehydration reaction.

2,5-Dimethyl-4-hydroxy-3(2H)-furanone and 2,4-dihydroxy-2,5-dimethyl-3(2H)-furanone can be produced by MR for pentose or hexose, or by 2,3-Dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one decomposition due to hexose reaction. 2,4-dihydroxy-2,5-dimethyl-3(2H)-furanone is particularly sensitive to oxidative decomposition reactions (Blank & Fay, 1996; Kim & Baltes, 1996). 2,5-dimethyl-4-hydroxy-3(2H)-furanone was detected in MTFPS, with 2,4-dihydroxy-2,5-dimethyl-3(2H)-furanone at lower levels for each treatment group.

1-(2-furanyl)-Ethanone MR product can be generated by Amadori compound degradation by Strecker, or dehydrated from 1-deoxy-2,3-

hexanedulose to form a dideoxyhexadiulose. This compound is cyclized, removing 2 water molecules to form 1-(2-furanyl)-Ethanone (Wnorowski & Yaylayan, 2000).

The findings confirm that pepper powder and raw materials undergo MR in the frying system, where MR product HMF is odorless and furanone and 1-(2-furanyl)-Ethanone have a caramel taste but higher threshold value, which may have little contribution to overall MTFP flavor.

Maillard treated fried pepper sauce differences by chemometrics

We determined correlations between main volatile substances for each MTFPS and acrylamide content changes and their contribution (Wang, Yang, He, et al., 2019). Fig. 4 shows characteristic compounds with large response values and acrylamide content for PLS-DA modeling. Yellow icons in Fig. 4 represent specific samples, and the rest are characteristic compounds.

Most characteristic compounds are located between r^2 50% and 100% ellipse. Groups A and D are in the third quadrant, i.e., positively correlated with 4 characteristic compounds and acrylamide, and negatively correlated with the other 31 compounds; Groups E, F, G, and H are located in the second quadrant, with dominant compounds (typical MR products 2,3-Dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one) and 6 characteristic compounds positively correlated, and negatively correlated with acrylamide. Group E has the highest correlation; and groups B and C are located in the first quadrant, i.e., positively correlated with 9 characteristic compounds. Group I is located in the fourth quadrant, i.e., positively correlated with 15 characteristic compounds, negatively correlated with acrylamide, and positively correlated with acetic acid. Group J is near the origin, indicating no characteristic compounds with high correlations.

Characteristic compound differences for each group reflects the different VOCs and acrylamide from different Maillard matrices. Group A (conventional auxiliary material group) and D have strongest acrylamide hazards and least volatile substances, whereas the other groups have relatively weak acrylamide hazards; Groups E, F, G, and H have similar effects and all have typical MR aroma. Typical aroma for groups B, C, and I is weaker, but the flavor level is more abundant, with group I lipid oxidation level being somewhat higher; Although acrylamide in group J is not very harmful, it is less relevant to VOCs with large response values. Thus, controlling acrylamide content in FPS can be achieved by exogenous MR treatment.

Fig. 5 shows calculated MTFPS volatile flavor compounds for substances with ROAV ≥ 0.1 . Exogenous Maillard treatment is commonly used to flavor food during processing, with different and volatile flavor substances produced by different substrate treatments. There were 32 substances with ROAV ≥ 0.1 , mainly aldehydes. Aldehydes have low fragrance threshold, which plays an important role in the overall product fragrance. Although ROAV for other types is not high, it enhances FPS aroma richness. This study believes that components with $0.1 \leq \text{ROAV} < 1$ have important modifying effects on overall sample flavor, and components with ROAV ≥ 1 are key flavor compounds.

Key flavor compound differences reflect their respective flavor properties, and maximum ROAV has major contribution to FPS flavor. There were 11 key main flavor compounds with ROAV ≥ 1 from the 10 FPS treated groups with different Maillard substrates. Flavor characteristics for each compound were shown in Table 2, and determined as described elsewhere (Avsar, Karagul-Yuceer, Drake, et al., 2004; Liu, Wang, Zhang, et al., 2019; Tian, Shi, Zhang, et al., 2019).

Group A has the fewest key flavor compounds (2), where main flavor is fresh and fat; Groups F and I have the most diverse composition (8 types), and they present a complex aroma of fatty, grassy, green, fruity, Dark chocolate, Rosey, and floral. Group F has prominent fruity aroma, whereas group I has prominent fatty, fresh aroma; Groups B, G, H, and J all have 3 key flavor compounds. The key flavor compounds in Group B presenting fatty, fresh, green, Rosey, floral, with a refreshing fatty taste;

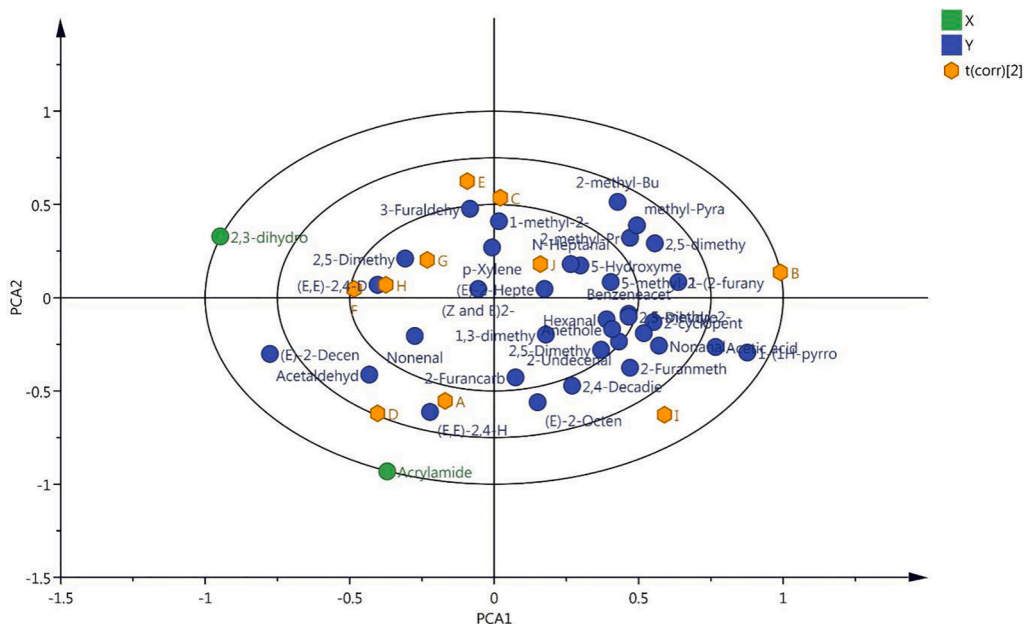


Fig. 4. PLS-DA outcomes for different Maillard treated fried pepper sauce (MTFPS): (A) sugar and sodium glutamate, (B) xylose and glycine, (C) xylose and cysteine, (D) xylose and soy peptides, (E) lactose and glycine, (F) lactose and cysteine, (G) lactose and soybean peptide, (H) sugar and glycine, (I) sugar and cysteine, (J) sugar and soybean peptide.

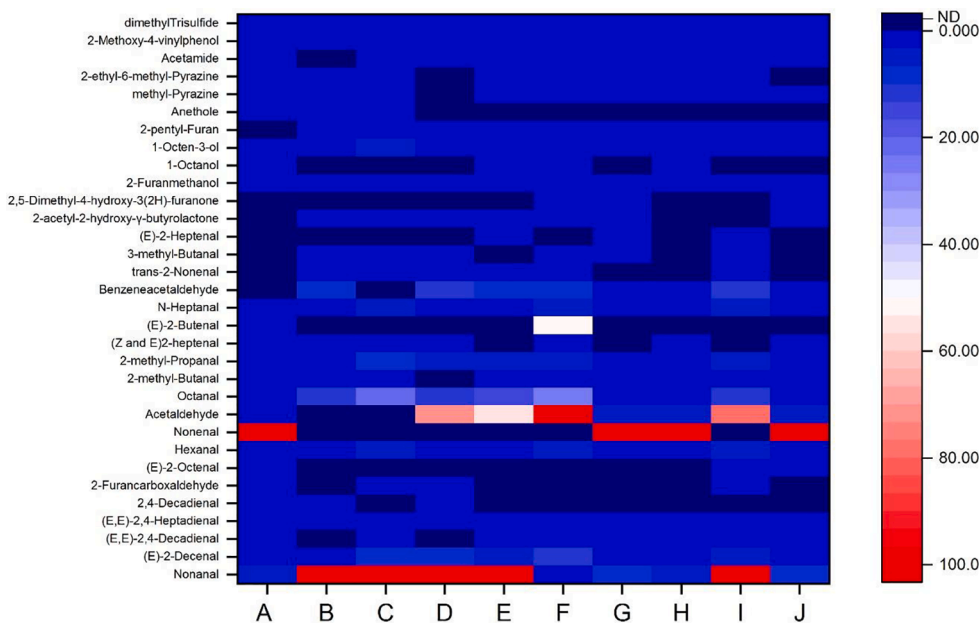


Fig. 5. Aroma compounds with ROAV > 0.1 in fried pepper sauce: (A) sugar and sodium glutamate, (B) xylose and glycine, (C) xylose and cysteine, (D) xylose and soy peptides, (E) lactose and glycine, (F) lactose and cysteine, (G) lactose and soybean peptide, (H) sugar and glycine, (I) sugar and cysteine, and (J) sugar and soybean peptide. ND Represents Not Found in treated fried pepper sauce.

and groups G, H, and J all have unpleasant fatty, fresh, fruity flavors, and prominently fatty. Groups C, D and E are consistent with 6 key flavor compounds. Group C have fatty, fresh, green, unpleasant, grassy, dark chocolate, and mushroom aromas; groups D and E have fatty, fresh, unpleasant, fatty, fruity, fatty, green, dark chocolate, rosy, and floral flavor. Group D fruity flavor is more prominent than that of group E; Therefore, differences in key flavor compounds for each group cause different MR flavor enhancements and different main flavor qualities.

We identified 21 modified volatile flavor substances in each treatment group with most exhibiting $0.1 \leq ROAV < 1$, including (E,E)-2,4-Decadienal, (E,E)-2,4-Heptadienal, 2,4-Decadienal, etc. There were 23,

19, 17, 15, 17, 18, 21, 19, 16, and 20 modified volatile flavor substance types in the 10 groups. Although ROAV differences for the modified flavor compounds do not fluctuate much, they have their own characteristic aromas. For example, anisene has anise aroma, whereas (E)-2-heptenal and (E,E)-2,4-heptadienal have fat aroma, etc. (Sun, Ma, Sun, et al, 2020). Although the groups A, B, G, H, and J have fewer key flavor compounds, it has more modified flavor compounds. The groups C, D, and E are in the middle, and F and I groups have more key flavor compounds, where group F has more modified flavor compounds and group I has less. Thus, all treatment groups have rich overall aroma quality, with different main aroma between groups, and slight

Table 2
Odor Descriptions in the Determination of Aroma Compounds with ROAV ≥ 1 from fried pepper sauce.

Count	Compound	odor description	Related group ^a
1	nonanal	fatty, fresh	A, B, C, D, E, G, H, J,
2	(E)-2-Decenal	unpleasant, fatty	C, D, E, F, I,
3	Hexanal	grassy, green, fatty	C, F, I
4	nonenal	unpleasant, fatty	A, G, H, J
5	acetaldehyde	fruity	D, E, F, G, H, I, J
6	octanal	fatty, green	B, C, D, E, F, I
7	2-methyl-Propanal	Dark chocolate	C, D, E, F, I
8	(E)-2-Butenal	–	F
9	N-Heptanal	fatty, green	F, I,
10	Benzeneacetaldehyde	Rosey, floral	B, D, E, F, I
11	1-Octen-3-ol	green, mushroom	C

^a Represents the ROAV ≥ 1 in the treated fried pepper sauce with different Maillard substrates.

differences in compound aroma.

In short, each treatment group has different aroma base notes, and different complex aroma levels. Group A aroma is relatively single fresh and fatty taste. The groups B, C, D, E, and I present a fresh and fatty base note. Group B compound aroma is floral, whereas C is grass, dark chocolate, and mushroom; D and E groups are fruity, dark chocolate, and floral, with group D exhibiting more fruity aromas; group I has grassy aromas, dark chocolate, floral fragrance; Group F has fruity base note, including grassy, green, dark chocolate, rose, and floral; groups G, H, and J have fruity base note on an unpleasant fatty aroma. Therefore, processing different exogenous Maillard reaction substrates can enhance FPS aroma, while simultaneously reducing harmful acrylamide.

Conclusions

Fried pepper sauce is fried at high temperature to produce characteristic aromas and induce acrylamide production. The current study used conventional excipients (white sugar and sodium glutamate) as control. FPS acrylamide and volatile substance changes under different MR treatments showed that acrylamide detection levels in other groups were significantly lower than the conventional excipient group ($P < 0.05$), with the lactose and glycine group having the lowest detection amount.

Fried pepper sauce samples mainly contain 10 types of 110 volatile compounds, including mainly aldehydes, ketones, alcohols, furans and pyrans, acids, alkenes, hydrocarbons, pyrazines and pyrroles, esters, and others, identified by GC-TOF-MS. Volatile components included oil oxidation volatiles (nonanal and acetic acid); and Maillard reaction products 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-Ketone, HMF, maltol, furanone, 2,4-dihydroxy-2,5-dimethyl-3(2H)-furanone, 2-acetylfuran. Therefore, lipid oxidation and MR occurred during FPS frying. We used PLS-DA to determine correlations between main VOCs in each treatment group and changes in acrylamide content and their contribution to the sample. We found that Group A (conventional auxiliary material group) and Group D, acrylamide, have strongest hazards and least volatile substances, whereas the other groups have relatively weak acrylamide hazards. Groups E, F, G, and H have similar effects and all have the typical aroma of Maillard reaction; Typical aroma for groups B, C, and I is weaker, but flavor level is more abundant, whereas lipid oxidation degree in group I is higher. Although acrylamide harm in group J is not strong, it has little correlation with volatile substances with large response values, indicating that controlling acrylamide content in oil capsicum can be achieved through exogenous MR treatment.

We used ROAV to analyze the different MR treatment flavor groups. Each treatment group had different aroma base notes and different complex aroma levels. Group A aroma was relatively simple fresh fatty taste, whereas the groups B, C, D, E, and I present fresh and fatty base note. Group B compound aroma is floral, and group C is grass, dark

chocolate, and mushroom; D and E groups are fruity, dark chocolate, and floral, and group D has more fruity aromas; Group I exhibits grassy, dark chocolate, and floral aromas; Group F exhibits fruity base note, including grassy, green, dark chocolate, rose, and floral; The groups G, H, and J have fruity base note on an unpleasant fatty aroma.

Therefore, FPS aroma can be enhanced while simultaneously reducing acrylamide harm by processing different exogenous MR substrates.

CRedit authorship contribution statement

Yuting Song: Writing – original draft, Data curation, Formal analysis, Investigation, Visualization. **Zhuhong Ding:** Writing – review & editing, Supervision, Validation. **Yuzhu Peng:** Writing – review & editing. **Jiaying Wang:** Writing – review & editing. **Ting Zhang:** Writing – review & editing. **Yihong Yu:** Writing – review & editing. **Yi Wang:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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